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High Rate Deposition of Reactive Oxide Coatings by New Plasma Enhanced Chemical Vapor Deposition Source Technology

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Clear silicon dioxide and zinc oxide coatings are deposited at high rates using a new plasma chemical vapor deposition source. The new source overcomes previous PECVD problems associated with electrode coating and enables dense, uniform, adherent films on low temperature plastics. Using the source, thick, abrasion resistant SiOC coatings are deposited at over 1100 nm-m/min. The source physics is presented and film properties such as Taber abrasion, Crock meter, adhesion and optical clarity are reviewed.

Introduction

General Plasma has recently introduced a new linear plasma source for large area plasma enhanced chemical vapor deposition (PECVD) processes[1]. The new source overcomes prior technical hurdles limiting the use of PECVD as a large area coating process. Advantages to the new technology include exceptional deposition rate of metal oxide films, dense, high quality films and the ability to deposit on low temperature substrates.

While PECVD has been routinely used in semiconductor processing for many decades[2], it is less common in large area applications such as flexible web and inline glass coating. One problem limiting use of PECVD for these applications is that the reactor electrodes are coated along with the substrate. For instance, in a parallel plate RF reactor, the powered electrode is exposed to the PECVD process and receives a large portion of the deposition. In semiconductor applications this is countered by routine etch back cycles. In continuous processes like web or inline coating, frequent etch back cycles are not practical. For these applications it is important that the electrodes remain free from insulating buildup over the length of the process run.

Beyond electrode coating, the lack of a uniform, high density linear plasma source has kept PECVD out of contention with sputtering. Magnetron sputtering can be configured to deposit uniform films over wide substrates. Additionally sputtering is a relatively stable process and is well known in the industry. Sputtering is far from ideal though. Sputtering of metal oxides is slow, sputter targets are expensive, the process is electrically inefficient and sputtered films contain relatively high stress making thick films difficult to produce.

Our goal at General Plasma is to make large area PECVD a useful, economical process. To do this, a superior linear plasma reactor was needed that overcame past technical limitations.

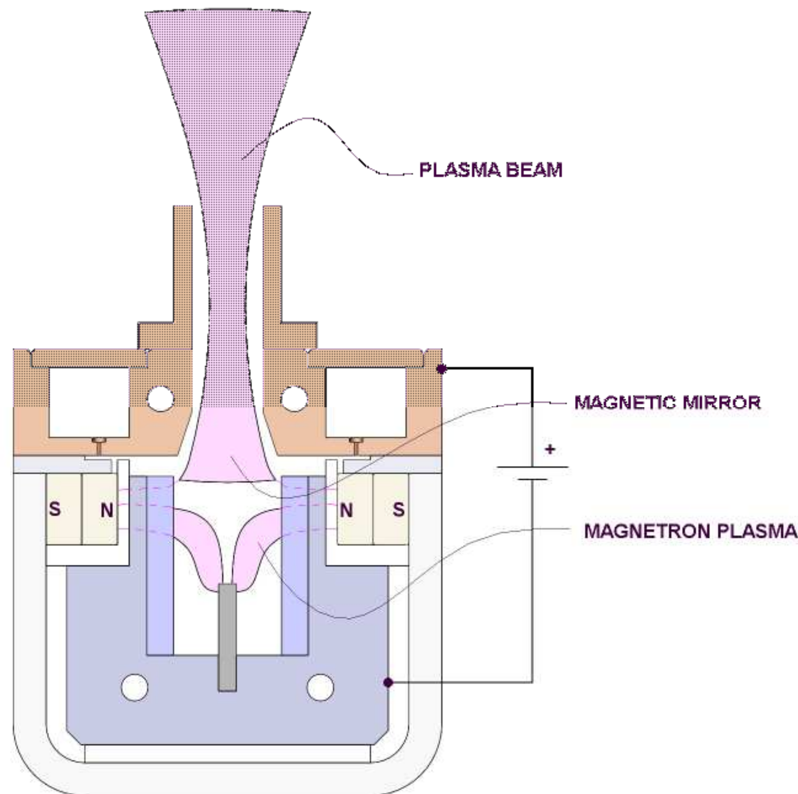

Fig. 1 Section View of Plasma Beam Source™

Dual PBS™ Technology

The Plasma Beam Source™ (PBS™) was introduced in 2002[3] and was applied to plasma cleaning in 2003[4]. This patent pending plasma source is a linear source that implements an internal magnetron cathode in a discharge cavity. Figure 1 shows a section view of the source and Figure 2 shows views of the PBS™ in action. Inside the discharge cavity the magnetron cathode forms a linear, uniform electron source. Through the judicious use of a cusp magnetic field, electrons are forced to exit the cavity though a reduced dimension nozzle. Gas injected into the PBS™ discharge cavity coincidently exits though the nozzle and is ionized by the high energy electrons. The result is a dense plasma which emanates from the source nozzle.

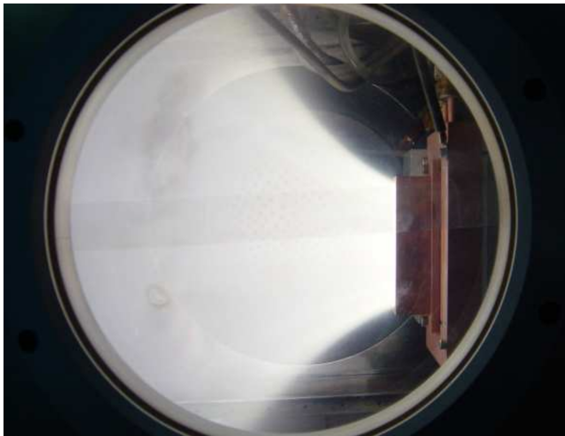

Figure 2A. Active PBS™ with Oxygen Gas

Figure 2B. End View of Active PBS™

When two PBS™ sources are combined across a mid frequency AC power supply, large area PECVD processes are enhanced. This configuration is termed the ‘Dual PBS™’. Figure 3 shows a schematic of this arrangement. Figure 4 shows a Dual PBS™ in operation.

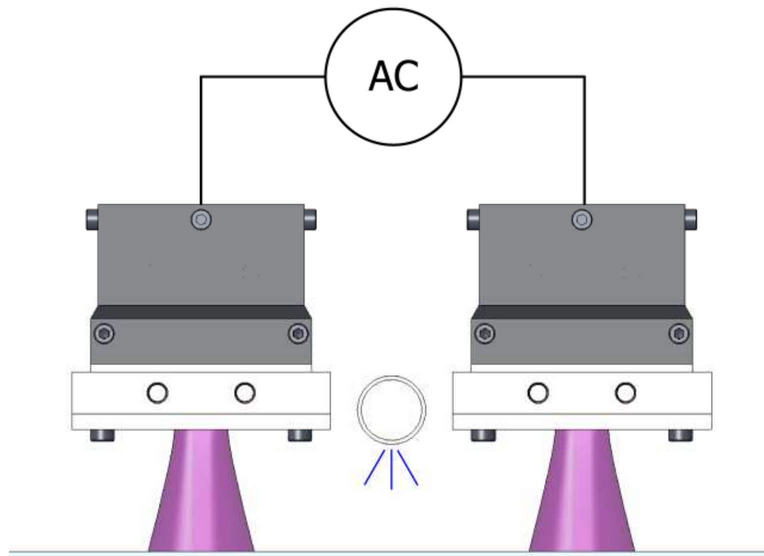

Fig. 3 Dual PBS™ Source Configuration

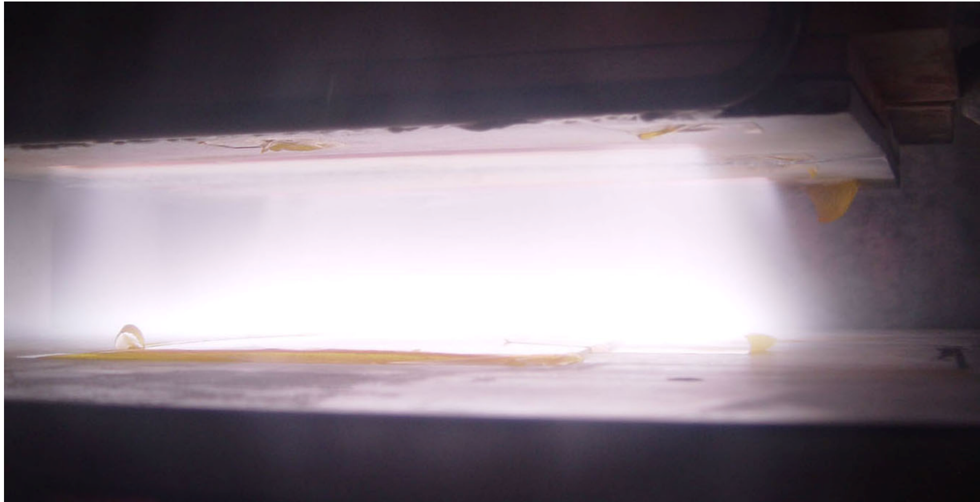

Fig. 4 Dual PBS™ Operating with HMDSO and Oxygen

With the Dual PBS™, each PBS™ alternates as the cathode and anode of the circuit. As the cathode, the PBS™ is a uniform, linear electron source. During this half cycle, the opposite PBS™ is the anode. Electrons leaving the cathode PBS™ must reach the anode PBS™ to return to the power supply. As the electrons attempt to enter the anode PBS™ nozzle, they encounter the mirror magnetic field emanating out of the nozzle. This impedes electron flow and generates an electric field in the nozzle. When gas atoms encounter these impeded electrons some are ionized and these ions experience the accelerating electric field. The result is a linear ion beam exiting each PBS™ during the anode half cycle. The ion energy is approximately 60-120eV. The plasma physics are similar to that of an end hall type ion source. While the ion beam is emanating out of the anode PBS™, the cathode PBS™ is providing neutralizing electrons. This dense, linear ion beam enables high quality PECVD coatings.

Latest Results

Dual PBS™ technology is being used to deposit films on a variety of flexible and rigid substrates including PET, PEN, polycarbonate, stainless steel and flexible solar cells (an emissive top coating). One of the challenges is to prove this new technology on large area substrates. Our R&D lab is equipped with 150mm wide nozzle PBS's. Sources with up to 350mm wide nozzles are operating in the field and are successfully depositing uniform, high quality films. We will soon be commissioning a new roll coater in our R&D facility with 400mm wide sources. The following section presents some of the latest Dual PBS™ results.

Silicon Oxide on PET

SiOx films were deposited on 127um PET web by Dual PBS™ and PECVD. The results for deposition rate tests are shown in Figures 5 and 6. The HMDSO precursor was delivered outside the sources. Oxygen gas was delivered through the sources. Power was held constant at 1500W. At 200 sccm of HMDSO the deposition rate was over 800nm-m/min. This rate shows improvement over sputtering of SiOx where typical deposition rates are 25-80nm-m/min. Figure 6 shows the haze of the coatings at the flow rates depicted in Figure 5. The low haze values indicate that clear, high quality SiOx films were deposited at all deposition rates. All samples exhibited clarity greater than 99.7%.

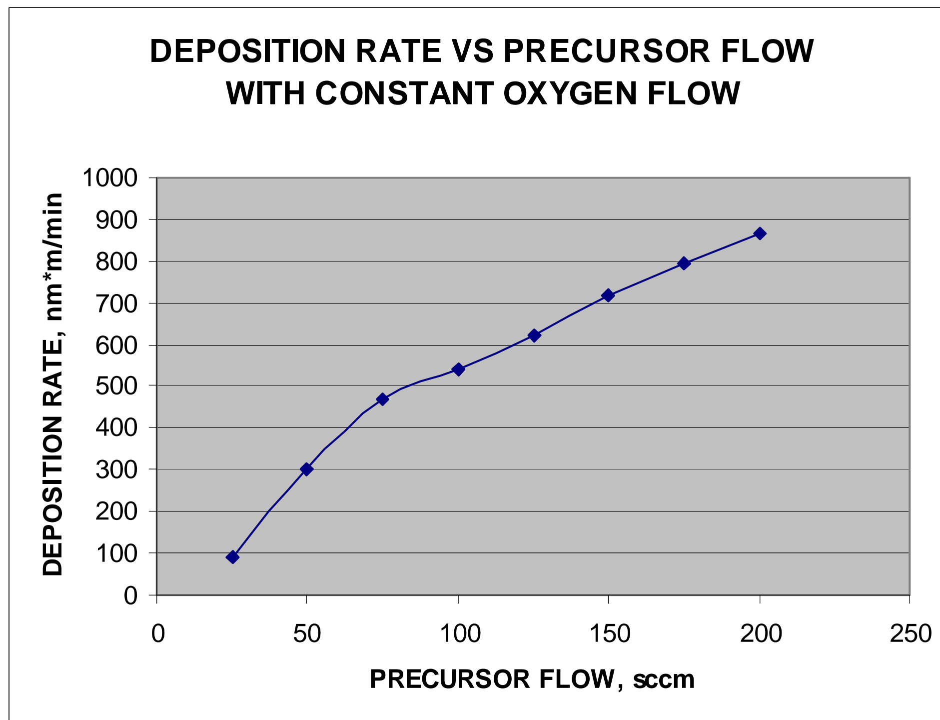

Fig. 5 Deposition rate vs. Precursor Flow of Dual PBS™

In coating each sample the deposition time was kept constant. Therefore, the coating thickness varied depending on the precursor flow rate. At the highest deposition rate the coating thickness was 3.6µm. For this film and all the thinner coatings the coating adhesion was excellent both before and after heat cycling. None of the samples exhibited any thermal damage.

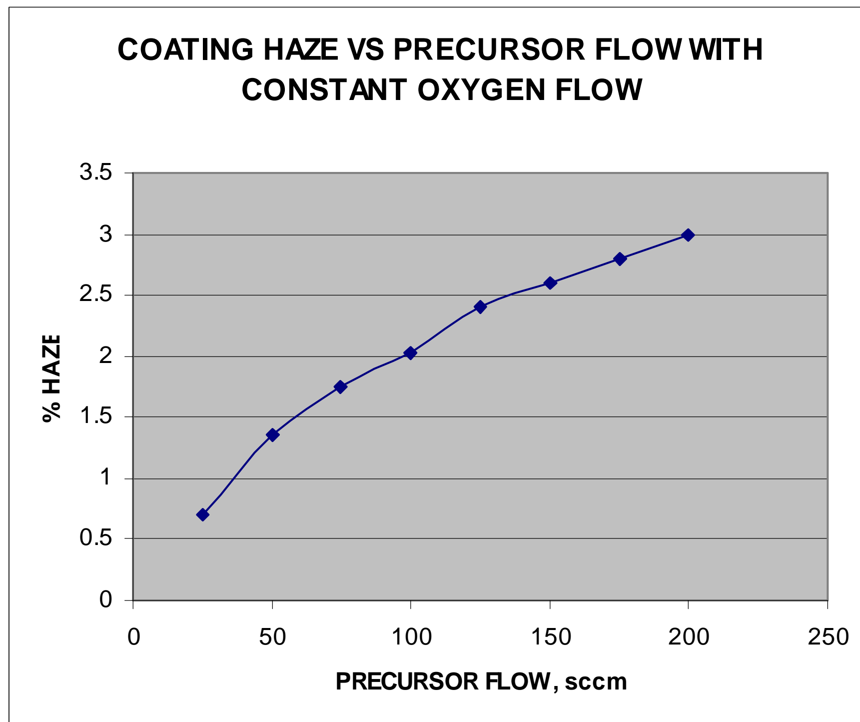

Fig. 6 Coating haze versus precursor flow (deposition rate)

Silicon Oxide on Polycarbonate

SiOx films were deposited on polycarbonate (PC) samples and the deposition rates were measured for a range of oxygen / precursor ratios. As the oxygen percentage was increased the deposition rate initially rose then subsequently dropped. Figure 7 shows the results for three HMDSO flow conditions. At 200 sccm HMDSO the AC power was 4000W. At 150 and 100 sccm HMDSO the AC power was 2000W. The PBS™ nozzle width was 150mm for both sources. Process pressures ranged from 35 to 100mTorr as oxygen gas flows changed.

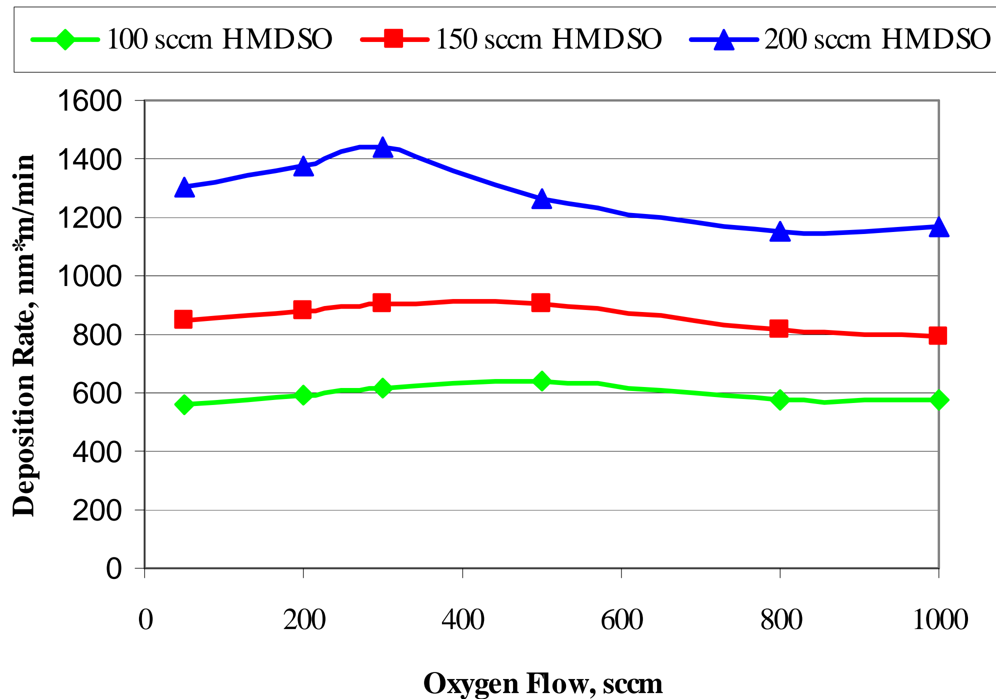

Fig. 7 Deposition rate of Dual PBS™ for 100 sccm HMDSO (diamond), 150 sccm HMDSO (square), and 200 sccm HMDSO (triangle)

The dynamic rate metric used, nm- m/min, indicates the thickness of a coating in nm if the substrate were to be translated past the sources at 1 m/min. For these deposition rate tests the substrate was mounted on a spinning drum 200mm in diameter. The circumference of the drum then is the coated length. In 5 minutes a 11.150 µm thick coating was deposited on the substrate. Therefore the static deposition rate is 11500 nm / 5 minutes or 2230 nm/min and the dynamic deposition rate is 1400 nm-m/min (11150nm*0.628m/5min). Dynamic deposition rate is the preferred measure as it is indicative of actual production potential.

Thick, silicon oxy-carbide films were deposited on PC to improve the abrasion resistance. The typical total coating thickness was 8 to 18 µm. Figures 8 and 9 show the results of Taber abrasion and crock meter testing on PC. The Dual PBS™ Taber samples were 18 µm thick. As illustrated in the graphs, the films are very abrasion resistant and have excellent post abrasion clarity. Film adhesion to the PC substrate passed ASTM D3359 both before and after boiling in water for 30 minutes.

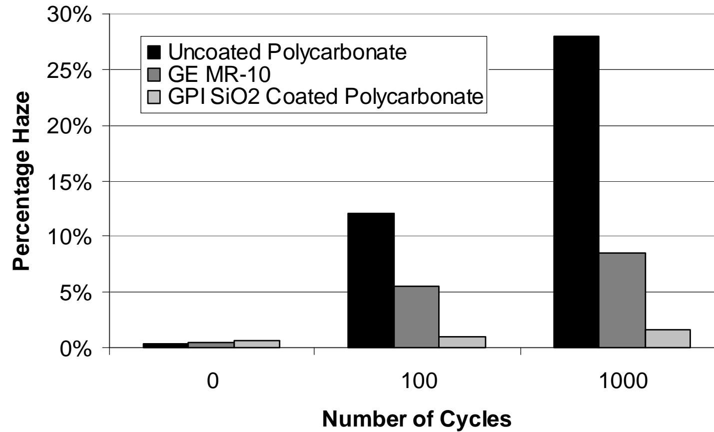

Figure 8 Taber Abrasion Haze Measurements on Polycarbonate (ASTM D 1044). Percentage haze was measured according to ASTM D 1003.

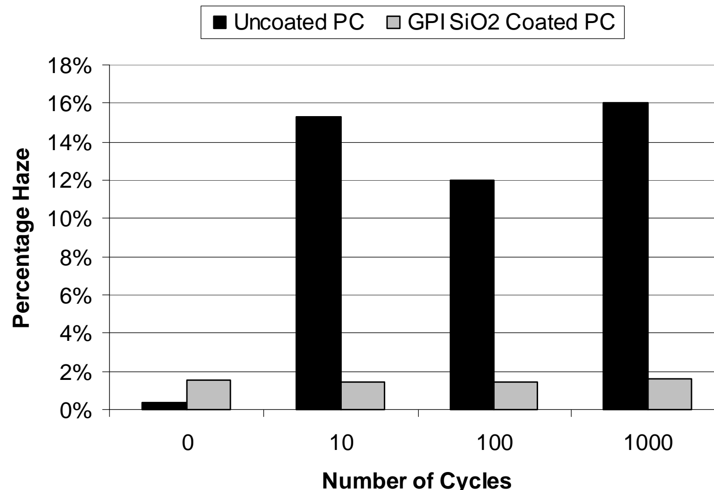

Figure 9 Crock Meter Haze Measurements on Polycarbonate (ASTM D 1044). Percentage haze was measured according to ASTM D 1003.

Zinc Oxide on Web

In a new development, ZnO films have been deposited on flexible web substrates. The films are clear and uniform across a 330mm wide web. Trimethyl zinc precursor is used with oxygen gas. Further data on this high index coating will be presented in a future publication.

Plasma Treatment of PET and PEN by PBS™

In addition to using the PBS™ technology for PECVD coating, a single PBS™ has been successfully implemented for pre-treatment of sputtered films[5].

Conclusion

PECVD by Dual PBS™ offers a new web coating technology. The technology's high deposition rate of over 1100 nm-m/min for SiO2 is significantly greater than either reactive sputtering or other linear PECVD methods. With the reporting of ZnO deposition by Dual PBS™ at this conference, both low and high index materials have been demonstrated. A brief list of possible applications for Dual PBS™ PECVD would include abrasion resistant coatings, barrier and encapsulation films, high and low index optical films such as color shift and anti-reflective coatings, transparent conductive films and emissive coatings.

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[2] Ludvik Martinu and Daniel Poitras, Plasma Deposition of Optical Films and Coatings: A Review, Journal of Vacuum Science and Technology, A 18(6), Nov/Dec 2000

[3] J. Madocks, Applied Process Technologies, Inc., New Magnetically Enhanced Source for High Rate PECVD, International Conference on Coatings on Glass, 2002 Proceedings

[4] J. Madocks, P. Marcus, Applied Process Technologies, Inc., Production of Atomic Oxygen for Reactive Deposition or Plasma Treatment Processes, Association of Industrial Metalizers, Coaters and Laminators, Fall Technical Conference 2003

[5] A. Klein, D. Wall, M. Shao, R. Bujas and R. Dunkel, General Atomics, Vacuum Coating and Technology, July 2005, pp34-39